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ANNUAL PERFORMANCE REPORT

**"Application of Stable Isotope Measurements to the Study of the Origin
and History of Meteorites"**

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A. Introduction

In the past year we have done a variety of researches dealing with the isotopic composition of hydrogen and carbon. We have applied our techniques to determine the isotopic composition of hydrogen and carbon in the Martian meteorites. Their unusual enrichment in deuterium is characteristic of the Martian atmosphere (Leshin et al., 1996). These results showed that deuterium analysis can be used as a definitive characteristic of a Martian origin. We have also continued our analysis of many Antarctic meteorites to ascertain their exchangeability with the light Antarctic water. This study should define their suitability to use these isotopic analysis as a criterion for their origin.

We have been involved with Dr. Ahrens group which deals with the effect of high energy impact on the chemical composition of crater materials. Our contribution involves the determination of the isotopic fractionation of carbon and hydrogen which would result from such impact induced volatilization. Oxygen isotope fractionation has already been observed in calcium carbonate (Boslough et al., 1982), serpentine (Tyburczy et al., 1990), serpentine and iron mixture (Faust et al., 1997) and the Murchison meteorite (Tyburczy et al., 1996). With the exception of Murchison, devolatilization has been accompanied by preferential concentration of light isotopes in the gas phases in both carbon and hydrogen. In the case of Murchison, the hydrogen in the gas phase was enriched in deuterium. These data provide some clues as to the possible isotopic partition between the solid Earth and the atmosphere due to the impact of meteorites. We plan to continue our cooperation in these experiments using a variety of starting materials, including alanine, which is our latest active project.

We have been able to extract organic compounds from a variety of meteorites with interesting results as to their origin. There are two classes of organic compounds available to us. One results from HF-HCl destruction of the inorganic compounds in meteorites which produces a mixture of a variety of organic materials (Yang and Epstein, 1983; 1984). We can also extract a specific organic compound from powdered meteorite using a specific solvent which allows us, for example, to identify deuterium enriched amino acid (Epstein et al., 1987; Pizzarello et al., 1994). We would like to continue this type of research using a large variety of meteorites.

B. The D/H and $^{13}\text{C}/^{12}\text{C}$ ratios of SNC Meteorites

1. Results of Last Year's Activities

Our research on the SNC meteorites was particularly rewarding because we were able to identify a characteristic of SNC meteorites which is strongly associated with the Martian origin. It is well established that the hydrogen associated with Martian materials should be highly enriched in deuterium. This then should be a required label for any organic or hydrous inorganic Martian compounds. It is very interesting that unlike our previous observations for meteorites, it is the inorganic hydrogen that is enriched in deuterium in Martian meteorites (Watson et al., 1994).

Our most recent results showed that large differences in the isotopic composition exists in the Martian meteorites. These δD values range between 500‰ to 4300‰. The lower 500‰ value, observed in the kaersutite, is significantly lower than that observed in the Martian atmosphere. This may indicate that the exchange history of the hydrous minerals with surface water on Mars is incomplete. The water extracted from SNC apatite has extremely high δD value of about 4000‰. One of the possible explanations for the high δD value of apatite is that it reflects more faithfully Martian surface water while the other hydrous minerals may have not formed on the Mars and still retained some of their original meteorite value. Another possibility is the isotopic composition of the Martian atmospheric water may have had a complicated history with respect to the isotopic composition. Originally, the water which entered Mars from outside may have been similar to our terrestrial water. The enrichment of deuterium in Martian atmosphere may have been taken many years and the present observed value is characteristic of only the present time. Thus the hydrogen in these hydrous minerals could have a large range of δD values depending on the time when they were formed and they may still reflect the true Martian isotopic composition of water at the time of their formation.

We have analyzed 8 SNC meteorites by step-wise combustion and obtained the isotopic compositions of the total hydrogen and total carbon to get some idea as to the range in D/H ratio that exists among various meteorites. In all cases, we found deuterium concentration is well beyond the terrestrial values. For any a single meteorite the most enriched deuterium hydrogen fraction came from the high temperature fraction. It is obvious that the meteorite that we treated contains various components of terrestrial hydrogen. We would like to continue to identify the different sources of the unusually high deuterium hydrogen in the SNC meteorites.

We extracted the carbon from the SNC meteorites by heating the samples in the presence of oxygen and converting the carbon into CO₂. The isotopic composition of the carbon varies, with $\delta^{13}\text{C}$ values as high as +40‰, which is not a characteristic value for the majority of meteorites. We would like to measure the isotopic composition of different sources of carbon and try to isolate the source of the unusually high $\delta^{13}\text{C}$ carbon.

2. Proposed Research for Next Year

We hope to continue to analyze any new SNC meteorite that are discovered to establish the maximum range of the δD values in the waters extracted from them. A δD value larger than 5000‰ would indicate that the isotopic composition of the Martian atmospheric water may have had a complicated history.

It is important to follow up the results we have obtained with as many SNC samples as possible. As our data already indicated water from different sources in SNC samples are highly variable. Martian water probably originated from extraterrestrial materials whose δD values could be very high or at an average not too different from terrestrial hydrogen whose origin is also extraterrestrial. Another source of hydrogen would be from the solar wind which is depleted in deuterium. The isotopic composition of Martian water may also be complicated by the dissociation of water and preferential escape of the lighter isotope of hydrogen. Consequently, extensive investigation of various source of hydrogen in SNC meteorites as well as other meteorites may give us some hint about the complicated history of the Martian water. The isotopic investigations of both hydrogen and carbon in SNC meteorites should be continued.

Nearly all of the SNC meteorites contain carbon which was extracted in the presence of oxygen as CO₂. We observed that some of carbon that was released at the high temperatures has $\delta^{13}\text{C}$ values as high as +40‰, which is not characteristic of the majority of meteoritic carbon. We would like to do a special experiment on one of the SNC meteorites (probably Nakhla) to determine the source of carbon. Although it is likely that the CO₂ that has been extracted from this meteorite originates from CaCO₃ it is important to determine whether any of the carbon has an alternative origin. We propose to dissolve a small sample of Nakhla with HF-HCl solution to remove the silicate as well as the CaCO₃. The residual material could then be carefully oxidized at various temperatures up to over 1000°C. The δD of the hydrogen as well as the $\delta^{13}\text{C}$ of CO₂ produced could be determined. Both the hydrogen and carbon could be isotopically unusual. The carbon could come from SiC which should have a high combustion temperature and an unusually high $\delta^{13}\text{C}$ value. This carbon may also be of a different origin which may have some

significance, such as the possibility that some organic chemistry has taken place on the surface of Mars. Our Mass Spectrometers can handle as little as 1 μ mole of hydrogen and 0.2 μ mole of CO₂. We would have to miniaturize our chemistry extraction particularly for the extraction of hydrogen, and consequently we would make preliminary runs with materials of known concentration and isotopic composition of hydrogen and CO₂.

We hope that our extensive past experience will qualify us to carry out similar hydrogen and carbon isotope analyses on the special meteorite ALH84001 or the equivalent.

C. The Isotopic Compositions and Concentrations of Gases Produced by Impact Devolatilization

1. Results of Last Year's Activities

This isotope project involves collaborative research with Prof. Thomas Ahrens. The ultimate goal of this collaboration is to determine the relationship between the isotopic composition of the gases injected into the atmosphere and the isotopic composition of the incoming meteorites that impact the Earth. We have previously published two papers, one concerning the fractionation associated with the devolatilization of calcium carbonate (Boslough et al., 1982), and the other dealing with the same process involving serpentine (Tyburczy et al., 1990). Our most recent manuscript (Tyburczy et al., 1996) describes the experiment in which the Murchison meteorite was subjected to the shock-induced devolatilization. The $\delta^{13}\text{C}$ and δD analyses were made on the original pieces and on the residue of the shocked sample. The results showed that the light hydrogen isotope and the heavier ^{13}C isotope were preferentially volatilized due to the impact. The reason for this seemingly ambiguous result may be due to the isotopic composition of the different sources available for shock-induced devolatilization. Since the dominant source of hydrogen is found in the hydrous minerals, which has a relatively uniform isotopic composition, it seems that the actual shock preferentially devolatilizes the lighter hydrogen. In the case of the carbon, there is a possibility that the preferential devolatilization of the ^{13}C may be due to the difference in the isotopic compositions of the different compounds. For example SiC has an unusually high $\delta^{13}\text{C}$ value (Yang and Epstein, 1984).

Another experiment involved using mixtures of serpentine and iron as target in shock-induced devolatilization research. The recovered residual solid is enriched in deuterium over the starting material indicating that hydrogen is preferentially partitioned into the evolved gas during impact devolatilization. This result is consistent with the

previous shock-induced D/H fractionation studies of serpentine and Murchison (Tyburczy et al, 1990; 1996).

2. Proposed Research

The most recent experiment for which we have preliminary results involve the amino acid L-alanine decomposition by impact-shock. It is of interest to determine how well organic compounds will survive the terrestrial impact of meteorites and to what degree they would be modified by this process. The initial results indicated that most of the L-alanine survived at a impact speed of 0.9 km/sec. However, additional experiment will be done involving L-alanine with different impact velocities. In addition, other amino acids will also be tested for their durability to the shot treatment subjected on them. We have constructed a line which will accommodate the extraction of gases formed by the impacts and the separation of the gases into the various component for isotopic analyses. Naturally, the isotopic analyses of hydrogen and carbon will be made and compared to the initial isotopic value of the starting materials in all experiments.

The other experiments planned will be the shock-induced devolatilization of a sample of the Murchison meteorite but at a lower pressure. Because there are large differences in the $^{13}\text{C}/^{12}\text{C}$ ratios in the different compounds in the Murchison meteorite, it will be possible to ascertain which of these components contributes to the atmosphere created by the shock-induced devolatilization. For example, the more refractory organic matter have δD values as high as 3000‰, when the δD of the OH groups in the hydrous minerals are close to -100‰ (Yang and Epstein, 1984). The $\delta^{13}\text{C}$ of the silicon carbide in the Murchison meteorite has a $\delta^{13}\text{C}$ value of 1500‰. The rest of the organic matter have $\delta^{13}\text{C}$ values typically of approximately -10‰. In the future, we hope to perform devolatilization experiments with regular heating on pure compounds and compare the isotopic fractionations in this process with those associated with shock-induced devolatilization .

D. The D/H and $^{13}\text{C}/^{12}\text{C}$ Ratio of Organic and Inorganic Materials in Antarctic Meteorites

1. Results of Last Year's Activities

In past years, we isolated the hydrogen and carbon of the organic matter from the carbonaceous and unmetamorphosed meteorites, and showed that the organic matter in meteorites is highly enriched in deuterium (Yang and Epstein, 1983). The hydrogen in the

inorganic fractions in the meteorites which are soluble in HF-HCl solution is isotopically similar to terrestrial hydrogen (δD value = $\sim -100\text{‰}$), including the inorganic fractions measured for the “falls” where exchange between the meteorite hydrogen and the atmospheric water is least likely. Also, the inorganic hydrogen in the hydrous minerals is the dominant source of hydrogen in the meteorites. Since the D/H ratio in the inorganic hydrogen is similar to terrestrial value it is important to determine that if this D/H ratio is due to its exchangeability. This type of information may provide some clues about the conditions that existed in the solar nebula during the period of time in which the hydrous minerals were formed. The Antarctic meteorites are the best candidate to test the exchangeability of the inorganic hydrogen because the δD value of the water in the ice cap, in the locations where the meteorites were found, is approximately -450‰ and the meteorites there could have been exposed to this source of water for about a million years. If permanent exchange took place in the δD of the Antarctic meteorites, then their δD values should be considerably lower than the δD values of the H_2O extracted from the meteorites which have been collected either as “falls” or “finds” in the continental United States. An unusual negative δD value for the inorganic hydrogen in meteorites would then serve as evidence that the δD values of the hydrous minerals in the meteorites must be considered more carefully as to their possible solar nebular origins.

Analyses were performed on 15 meteorites, nine of which came from the Antarctic, and six of which were divided equally between “falls” and “finds.” Stepwise combustion of the 15 meteorite powders were done in six successive temperature steps, 50, 150, 250, 350, 700, and 1000°C . The hydrogen isolated from these different steps show no unusual low δD values which would indicate the lack of influence by the Antarctic waters. The next step was to determine whether the meteorites under consideration contain significant amounts of organic hydrogen and carbon with unusual isotopic compositions. Acid residues were prepared for 9 meteorites: 7 from Antarctica, Sharps, and Murchison. Both the ordinary and carbonaceous chondrite residues release the bulk of their hydrogen during the 350°C step and in all cases deuterium is enriched in the residue relative to the bulk sample. Among the ordinary chondrites two had very strong deuterium enrichments ($\delta D > +1500\text{‰}$) in the high temperature steps, while two had relatively minor δD enrichments ($+200\text{‰}$), an one failed to give enough hydrogen for isotopic analysis. The acid residues from the two CM chondrites are also characterized by a relatively high δD enrichment ($+600\text{‰}$ to $+800\text{‰}$) which is relatively constant as a function of extraction temperature.

A highly variable fraction (7-99%) of the total carbon present in the meteorites is recovered in the acid residues which typically release increasing amounts of C with

increasing temperatures of extraction. The $\delta^{13}\text{C}$ values of the acid residues do not differ dramatically from bulk $\delta^{13}\text{C}$ values, except in the low temperature fraction from Antarctic meteorite acid residues which has $\delta^{13}\text{C}$ values between -30 and -25‰ rather than the elevated values (>-15‰) characteristic of the bulk Antarctic meteorites.

Another approach was taken to determine why the δD of hydrogen showed no sign of a contribution of Antarctic water. This was to perform isotope exchange experiments in the laboratory. We subjected powdered Clovis and Murchison meteorites to interaction at room temperature with water whose δD value is -400‰. Our technique was to simply exchange the powdered meteorite with a large excesses of the isotopically unusual water in sealed glass capsules at different thermostated temperatures. After the required time for exchange has passed, the total mixture of powder and water was quenched rapidly to about -1°C. At this time, the water in the system was removed by freeze-dry techniques which allows the removal of water without effecting its isotopic composition, and permits the analysis of the dried and exchanged hydrous minerals for their δD values. Within one day, the waters extracted from Clovis had δD value which was essentially -260‰ at all temperatures of extraction, ranging from 50 to 350°C. Clovis released very little water at temperatures higher than 350°C. These results of one day exchange experiment differed very little from the one which was carried out for 34 days. This result clearly indicates that there is a highly exchangeable component in Clovis which will not preserve a δD value acquired in the Antarctic environment once it was removed from that environment. The Murchison exchange experiment showed that up to 350°C the δD of the waters extracted is similar to those of Clovis, but at 350°C and higher temperatures the δD of extracted water is very similar to the original hydrogen extracted prior to the exchange experiment, indicating this fraction of water is not readily exchangeable at room temperature. The percentage of exchangeable meteoritic water can also be determined by exchanging the meteorite with three or four waters with markedly different isotopic compositions using the material balance equation. For example, the results for Clovis indicate that roughly 50% of its water exchanged very rapidly with the surrounding liquid water.

2. Proposed Research

One of our objectives in doing this work was to identify interesting Antarctic meteorites which could be used for our various researches. For example, carbonaceous meteorites contain compounds which can provide information about their sources and can be relevant to the origin of life on the Earth. We will continue to test various available samples in the Antarctic collection which can be used for such purpose.

We want to prepare acid residues using meteorites which contain relatively high proportion of hydrogen and carbon in the fraction released at temperatures of 350°C and above. Samples ALHA 77299, 77214, 77307, 81002, Willaroy, Ragland provide potential sources of extraterrestrial organic matter whose δD and $\delta^{13}C$ would be informative as to their origin.

Also we want to determine the fraction of unexchangeable hydrogen by our technique described above using some of the other meteorites. It would be interesting to establish this technique as a way to identify various type of water present in meteorites. For example, exchange experiment can be done at various elevated temperatures to determine if the degree of exchangeability is affected by temperature. A stepwise change in the exchangeability with temperature may be used to characterize certain source of water if preliminary experiment is done with artificial mixture of hydrous compound which has been identified in meteorites.

In summery, we have shown that one can determine the D/H ratio and concentration of the exchangeable water by subjecting a known weight of meteorite powder with a water of known isotopic composition. This exchange experiment can be repeated at different temperatures to ascertain if there are different types of exchangeable hydrogen present in the meteorites which can be exchanged to different degree depending on the temperature. If there is no temperature effect on the degree of exchangeability of the hydrogen in meteorite this would be a very important result.

We would also wish to create more HF-HCL residues from the Antarctic meteorites which have been shown to have materials enrichment in δD and $\delta^{13}C$. Indeed, it may be interesting, as a matter of course, to test a small sample from a large variety of Antarctic meteorites to provide such information to the scientific community as part of our research program. For our own research, the identification of carbonaceous and SNC meteorites among the Antarctic meteorites would be of special interest to us.

E. The δD , $\delta^{13}C$ and $\delta^{15}N$ Values of Specific Organic Compounds Extracted From Murchison

1. Introduction

For the past several years, we have used D/H and $^{13}C/^{12}C$ ratios of the hydrogen and carbon in organic materials as an indicator of the origins of a variety of classes of organic compounds extracted from the Murchison meteorite (Cronin et al., 1993, enclosed;

Pizzarello et al., 1991; 1994). For example, the δD value of amino acids ranged from 1000‰ to 2500‰, as compared to the much lower range of values between 100‰ and 500‰ for the aliphatic and aromatic hydrocarbons, and the intermediate range of 350‰ to 900‰ for the polar hydrocarbons and methanol extracts (Krishnamurthy et al., 1992). All of these were done in cooperation with Dr. Cronin at ASU.

2. Proposed Research

We would like to resume these extractions of the components described in the paper of Krishnamurthy et al. (1992) from meteorites other than Murchison. For example, we will apply this extraction techniques on SNC meteorites using the same solvents. These extraction should give us sufficient information as to the origin of the extracted components. Presumably a deuterium enriched organic compound would provide strong evidence for the formations of these compounds in a Martian environment. Any evidence of such deuterium enriched compounds which can be assigned to a biological process would be most exciting and warrant a considerable attention.

F. SO₂ Weathering on Io

Dr. Burnett and his group have been doing experiments to determine the erosion processes of SO₂ on silicate surfaces. These experiments involved contribution of our laboratory. A manuscript reporting these results is being reviewed for publication by the Journal of Geophysics Research (Burnett et al., 1997). This experiment was done in order to explain the high concentrations of sulfur and sodium on the surface of Io. In one experiment, soda-lime glass was heated with pure SO₂ in a sealed quartz tube. This was repeated on the albite-SO₂ system. By observing the surface of the silicate which has been interacted with SO₂, it was shown that SO₂ disproportionation as well as direct formation from SO₃ under oxidizing conditions can produce Na₂SO₄ by interaction of SO₂ with silicates. Ca and Fe sulfates may form preferentially in more basaltic compositions. As highly oxidizing conditions may be unlikely for Io, the disproportionation mechanism may be more competitive on Io than it is in laboratory experiments. Very low rates of Na₂SO₄ production are required to supply the Io atomic cloud, so the interaction processes can be very inefficient. SO₂ disproportionation is a possible origin for S on the surface of Io.

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